SYNTHESIS OF ASYMMETRIC POLYETHERIMIDE MEMBRANE FOR CO_2/N_2 SEPARATION

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UNIVERSITI SAINS MALAYSIA
2017

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by

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Thesis submitted in fulfilment of the requirement

The degree of Master of Science

July 2017

ACKNOWLEDGEMENT

All praises are due to almighty Allah, the lord of the universe, the most beneficent, and the most merciful. This thesis would be dedicated to my beloved mother, late alhaja Silifat Adunni, as well as my beloved wife, Mariam Abidemi.

Then, I wish to express my sincere gratitude and appreciation to my advisor, Professor Abdul Latif Ahmad, a great scholar, educator, and mentor, for his direction, support, and inspiration throughout the development of this research work. My sincere gratitude also goes to my Co-supervisor, Dr. Zeinab Abbas Jawad for her effort and patience throughout the journey of the research.

Thanks to all the administrative staffs and laboratory technician of School of Chemical Engineering, USM, for their friendly help and support without any reluctance. This acknowledgement will not be completed without appreciate my friends, colleague, especially my roommate, Mallam Kabir Garba for their companionship and helpful advice.

To those who contributed indirectly to this research work, your kindness means a lot to me. I say thank you all.

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LIST OF SYMBOLS

Symbol	Description	Unit
P	Permeability coefficient	cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$
D	Diffusion coefficient, which represents the mobility of the gas through the membrane	cm^2 s^{-1}
S	Solubility coefficient	cm^3 (STP) cm^{-3} $cmHg^{-1}$
C_D	concentration of gas in the polymer matrix	
K_D	Henry's Law constant	
C_H	Standard Langmuir adsorption	
Å	kinetic diameter	
J	flow rate of a component through the membrane	
ΔP	driving force	bar
l	membrane thickness	µm
p	Membrane permeance	GPU
A	Membrane effective area	cm^2
h	hydrogen-bonding	
d	Dispersive bonding	
p	Polar bonding	
t	Total bonding	
P_A	Permeability of fast gas (CO_2)	Kmol.m/m^2 .s.bar

LIST OF ABBREVIATION

CO_2	Carbon dioxide
CO	Carbon monoxide
CCS	Carbon capture and storage
CDM	Clean development mechanism
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
FTIR	Fourier transform infrared
GHGs	Greenhouse gas
H_2O	Steam
H_2	Hydrogen
IPA	Isopropanol
KP	Kyoto Protocol
NMP	N-methyl-2-pyrollidone
N_2	Nitrogen
O_2	oxygen
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
PDMS	Polydimethylsiloxane
PC	Polycarbonate
PE	Polyesters
PEI	Polyetherimide
PES	Polyethersulfones
PI	Polyimides
PS	Polystyrene
PSA	Pressure swing adsorption
PSU	Polysulfones
PU	Polyurethane
PVDF	Polyvinylidene flouride
PVA	Polyvinyl acetate
PVC	Polyvinyl chloride

Rpm	Rate per minute
SEM	Scanning electron microscopy
T_g	Glass transition temperature
TMU	Tetramethylurea
TSA	Temperature swing adsorption
UNFCC	United Nations Framework Convention on Climate Change
U.S.A	United State of America
WGS	Water gas shift
XRD	X-ray Diffraction
Wt. %	Weight percent

SINTESIS MEMBRAN POLIETERIMIDA ASIMETRI UNTUK PEMISAHAN CO_2/N_2

ABSTRAK

Perubahan iklim menjadi cabaran global disebabkan oleh suhu permukaan bumi yang semakin meningkat. Fenomena ini menjadi semakin meruncing dengan perkembangan aktiviti perindustrian disebabkan oleh peningkatan pelepasan gas rumah hijau terutamanya CO_2. Ini menjadikan pemisahan CO_2 daripada gas serombong sebagai penyelidikan yang menarik berikutan peningkatan permintaan untuk tenaga dan keperluan untuk teknik pemisahan gas yang cekap tenaga dan mesra alam sekitar. Kebanyakan gas serombong dihasilkan bersama dengan CO_2 yang perlu diasingkan untuk persekitaran yang bersih.

Proses songsangan fasa kering-basah ialah salah satu teknik yang digunakan dalam tugas ini untuk memperbaiki prestasi membran. Teknik yang digunakan untuk proses songsangan fasa kering-basah adalah untuk menghasilkan permukaan membran yang padat tak simetri dan kurang berliang untuk menggalakkan pemisahan CO_2 yang lebih baik. Penggunaan masa berdiri bebas (FST) yang lebih tinggi sebelum direndam di dalam larutan penggumpalan dijangka mampu untuk menyelesaikan masalah ini.

Kepekatan optimum PEI polimer pada kepekatan 30 wt. %. Didapati dapat menghasilkan lapisan kulit yang padat, struktur seperti span dengan liang makro seperti jari yang seragam di sublapisan. Membran yang dihasilkan mempunyai ketelapan CO_2 sebanyak 500.2 GPU dengan kememilihan sebanyak 1.43. Kesan ketebalan acuan telah dikaji dan ketebalan acuan optimum diperolehi pada 300 μm. Pada ketebalan acuan yang lebih tinggi, liang makro seperti jari adalah minimum

dengan lapisan kulit tebal sebanyak 16.84 μm. Penggunaan penggumpal yang lembut seperti isopropanol menjurus kepada proses pemisahan tertangguh dengan lapisan kulit yang tebal dan struktur seperti span yang hampir lengkap. Membran ini memberikan ketelapan CO_2 sebanyak 5.49 GPU dan kememilihan CO_2/N_2 sebanyak 11.44. Selain itu, suhu larutan penggumpalan telah digunakan untuk mengkaji keadaan penggumpal yang membolehkan kememilihan CO_2 yang lebih tinggi. Pada suhu larutan penggumpal yang serendah 0 ^{0}C, struktur membran mempunyai struktur seperti span yang lengkap dengan ketebalan kira-kira 88.06 μm. Suhu larutan penggumpal yang rendah menggalakkan pemisahan membran pada keadaan ini dengan ketelapan CO_2 sebanyak 3.41 GPU dan kememilihan sebanyak 18.94. Sementara itu, terdapat pembentukan liang makro jejari pada suhu larutan penggumpal melebihi 30 °C dengan peningkatan ketebalan membran. Walau bagaimanapun, membran PEI dengan masa berdiri bebas (FST) sebelum rendaman ke dalam larutan penggumpal telah meningkatkan prestasi pemisahan CO_2. Membran ini, dengan 30 minit (FST) menunjukkan ketelapan CO_2 sebanyak 3.35 GPU dengan kememilihan CO_2/N_2 sebanyak 29.79. Membran ini didapati telah memperolehi kawalan yang baik dalam penghasilan membran PEI yang optimum bagi pemisahan CO_2.

Secara umumnya, keputusan keseluruhan menunjukkan membran PEI ini mampu menghasilkan kememilihan yang baik berbanding dengan polimer lain untuk pemisahan CO_2. Kesimpulannya, membran PEI setanding untuk pemisahan CO_2 dengan kememilihan yang baik.

SYNTHESIS OF ASYMMETRIC POLYETHERIMIDE MEMBRANE FOR CO_2/N_2 SEPARATION

ABSTRACT

The climate change becomes the global challenges due to the increasing earth's surface temperature. This phenomenon was aggravated by the expansion of industrial activities due to the increasing emissions of the greenhouse gas mainly CO_2. This makes the separation of CO_2 from flue gas attracted research interest due to increasing demand for energy and the need for more energy efficient and environmental friendly gas separation technique. Most of the flue gases are co-produced with CO_2 which needs to be removed in order to have a clean environment.

Dry-wet phase inversion process is one of the techniques that were adopted in this work to further improve the membrane performance. The adopted technique used to performed the dry-wet phase inversion is to have a dense asymmetric and a less pores at the surface of the membrane to allow a more selective CO_2. The use of higher free standing time prior being immersed in coagulation is expected to solve this problem.

The optimum PEI polymer concentration was found to be at 30 wt. %. At this concentration, the membrane has a dense skin layer, a sponge-like structure with uniform finger-like macrovoid at the sub-layer. The produced membrane has CO_2 permeance of 500.2 GPU with selectivity of 1.43. The casting thickness effect was investigated and the optimum casting thickness is found at 300 μm. At higher casting thickness, the finger-like macrovoid is minimal with a thick skin layer of 16.84 μm. The utilization of soft coagulant such as isopropanol leads to delay demixing with thick skin layer and almost complete sponge-like structure. This membrane gives

CO_2 permeance of 5.49 GPU and a CO_2/N_2 selectivity of 11.44. Also, coagulant bath temperature was used to study condition of coagulant that could favour higher CO_2 selectivity. At lower coagulation bath temperature of 0 °C, the membrane structure has a complete spongy-like structure with a thickness of approximately 88.06 μm. The lower coagulation bath temperature favours the membrane separation in this condition with CO_2 permeancce of 3.41 GPU and selectivity of 18.94. Meanwhile, there is development of finger-like macrovoid at higher coagulation bath temperature of 30 °C upward with increasing thickness of the membrane. However, PEI membranes with a free standing time (FST) prior immersion into coagulation bath improved the CO_2 separation performance. These membranes at 30 min (FST) showed CO_2 permeance of 3.35 GPU combined with a CO_2/N_2 selectivity of 29.79. These membranes were found to acquire good control in producing the PEI membrane for CO_2 separation.

Generally, the overall results showed the PEI membrane is able to produce good selectivity compared to other polymer for CO_2 separation. It can be concluded that the PEI membrane is comparable for CO_2 separation with good selectivity.

CHAPTER ONE

INTRODUCTION

1.1 Carbon Dioxide Capture

Although there is no universal agreement on the source of global climate change, the greenhouse gas (GHGs), the mainly anthropogenic carbon dioxide (CO_2) emission is considered widely as the major liable cause (Li et al., 2016). U.S. Department of Energy reported that approximately 83% of the GHGs emission recorded in the U.S.A. is ascribed to combustion of non-renewable fossil fuels. Hence, the capture of CO_2 would not only mitigate the global warming concerns but also have some economic benefits, since CO_2 can be utilized in enhanced oil and coal bed methane recovery (IEA, 2015). Thus different countries have taken different measures to control the rising rate of GHGs production globally. United Nations Framework Convention on Climate Change (UNFCC) is the nonbinding protocol aimed at atmospheric GHGs reduction which more than 150 countries are signatories to the protocol (Lund, 2006). The countries that participate in UNFCC in December 1997 adopted the Kyoto Protocol (KP). The KP agreement is a global convention to fight climate change by rapid reduction of GHGs in the world. The KP agreement is related to UNFCC in which Malaysia was registered as a country that ratified the KP by September 2002 being a developing, non-Annex I country (Xiao and Li, 1997). A new mechanism was formed in the KP which do not have any mandatory emission reduction target between the Annex I (industrialized) and non-Annex I (developing) nations which is the clean development mechanism (CDM) and this mechanism is cost-effective. The CDM idea allows the market to determine where it is economical to reduce emissions, which should remarkably lower the cost of compliance in the world. Malaysia being a non-Annex I country is affected by the CDM under the KP

agreement. CDM promotes joint or co-operative projects between developed and developing countries with the opportunities for additional monetary and technological investments in reduction of GHG projects (Oh, 2010). On the contrary, the Copenhagen Accord emphasizes on global GHGs stabilization, rather than suppressing the rise of earth's temperature (especially below 2^{o}C) so as to avert consequent dangerous sudden climate changes. Although they do not set global emission limits, however, they supported the view that global emission should be suppressed urgently and depending on whether the signatory countries fall in category of Annex I or non-Annex I, they should set their own emission limits targets either jointly or individually (Lau et al., 2012).

Currently, there are three major approaches to reduce CO_2 emission from fossil fuel; these are pre-combustion, oxy-fuel and post-combustion. The main principle of pre-combustion is to supply purified oxidizer fuels to the combustion turbine in order to reduce the heat loss generate by the inert gases (Leung et al., 2014). For example, in a typical incorporated gasification combined cycle power plant, the coal (fuel) is sent to the gasifier to produce hydrogen (H_2) and carbon monoxide (CO). By converting carbon monoxide to CO_2 by water gas shift (WGS) reaction generated H_2, then, fuel stream is sent to the gas turbine and the inert CO_2 should be extracted in order to achieve high electricity generation efficiency (Bernardo et al., 2009). Thus, the high temperature of the mixed steam, the thermal stability of the membrane module becomes critical. A polybenzimidazole (PBI) membrane developed by Los Alamos National Laboratory has shown long-term hydrothermal stability at 250 degrees for 350 days (Berchtold et al., 2006). Some inorganic membranes derived from ceramic, silica, metal, and by further doping or alloying are also competitive candidates for this high-temperature carbon

dioxide/hydrogen (CO_2/H_2) process. However, these inorganic membranes only allow H_2 to pass through, and CO_2 remains in the high-pressure retentate stream (Diniz da Costa et al., 2009).

Another promising technology is oxy-combustion, in which the fuel is burned with almost pure oxygen mixed with the recycle flue gas (Merkel et al., 2010). The advantage of this technology is that the exhaust is only CO_2 and water, which means the CO_2 can be compressed and stored after dehydration without spending energy on other inert gasses, for instance, nitrogen (Bernardo et al., 2009). Thus, nitrogen (N_2) has to be removed from the air to produce enriched oxygen (O_2) at the beginning of this process. The conventional way to remove N_2 from the air is cryogenic distillation because N_2 has higher a boiling point than O_2. However, researchers were working tirelessly to be cost-effective on oxygen generation by using membranes technology (Leung et al., 2014).

Post-combustion CO_2 capture has the greatest potential to be the near-term solution for reducing CO_2 emission from power plants because the captured CO_2 can be recycled to the existing conventional coal power plant (Merkel et al., 2010). However, lots of challenges have to be solved. For instance, the CO_2 content of the flue gas after combustion at atmospheric pressure, is around 10-20% with a partial pressure of 0.1-0.2 atm and the thermodynamic driving force for CO_2 capture is considerably low (Favre, 2007). Hence, the CO_2 captured by post-combustion is on the low-pressure side. Appropriate compression is therefore needed to meet the sequestration requirements (Liang et al., 2015). Meanwhile, the temperature of flue gas coming from a turbine is higher than 100 °C; in that case, heat exchange or additional cooling treatment is required. Amine-based absorption system is the mature and commercially available solution for the post-combustion capture. Amine

reacts with CO_2 to form reversible chemicals that could release the CO_2 at a higher temperature and lower pressure. The foremost advantage of the amine-based CO_2 capture system is that this absorption process can capture at a lower pressure compared to membrane process (Favre, 2007). Nevertheless, there are other problems like scale up, amine losses, degradation, and corrosion related amine absorption. Whereas, oxy-fuel and post-combustion process is mainly applied to both gas and coal fired power plants, pre-combustion is majorly applied in coal-gasification plants. The currently widely established process for CO_2 capture is the post-combustion technology (Bhown and Freeman, 2011). Meanwhile, membrane technology is considered as a feasible CO_2 separation method and more viable option compared to other conventional techniques in terms of cost, process safety, and environmental effects (Brunetti et al., 2010). However, membrane technology for CO_2 capture has only been investigated in details for pre-combustion application.

Therefore, the application of membrane technology for post-combustion process would require an effective membrane system equipped with features capable of overcoming aforementioned post-combustion barriers and also selective to other gaseous impurities (SO_x and NO_x gases) in the CO_2 (Brunetti et al., 2010).

1.2 Membrane Technology for Carbon Dioxide Separation

As discussed previously, the complications of global warming together with climate change are currently generalized and represented in terms of CO_2 emission by day to day human activities (Lahijani et al., 2015). Where, most of the world's primary energy requirement is driven by fossil fuels, which results in escalating emission of GHGs and consequent concerns over global climate change (Leung et

al., 2014). In addition, different concentration of CO_2 in flue gases largely depends on the fuel type and sources such as coal (12-15 mol % CO_2), natural gas (3-4 mol % CO_2), and oil refining (8-9 mol % CO_2) which must be removed. Typically, CO_2 is the primary source of GHG, accounting for 77% of the consequences of human activities in the recent decade. Drastic CO_2 sequestration and minimal emission from various gas streams can be achieved by exploring potential separations technology. Besides, CO_2 is a reactant and a building block for fine chemical synthesis in many chemical industries. As such, the consumption of CO_2 globally has surpassed 20 million tons per year and this is predominantly utilized by the CO_2 merchant market, chemical, beverages and food, and other process industries (Kargari and Takht Ravanchi, 2012). Nevertheless, either for utilization or storage, CO_2 must be separated. Currently, the widely employed CO_2 capture method involve reversible chemical and physical absorption while membrane processes are sparsely used; thus, they are attractive because of their energy efficiency and simplicity (Abu-Zahra et al., 2009). The fact that there are no yet appropriate technical solutions or technologies that can efficiently capture the CO_2 increase in the atmosphere has been a vast challenge to the researcher. In the membrane cluster, a membrane technology capable of working under a wide different conditions that have a substantial impact on the separation of CO_2 is desirable (Czyperek et al., 2009, Shao et al., 2009, Baker et al., 2008). Presently, membranes technology has become a recognized technology for CO_2 removal (Doshi, 1999). It has increasingly become a promising alternative technology for CO_2 capture, which has found favourable application in various methods such as membrane gas absorption, facilitated transport membrane, and membrane gas separation (Brunetti et al., 2010). However, in order to reduce the

total cost of CO_2 capture and environmental impacts, priority is given to those technologies with improved CO_2 removal efficiency.

In addition, membrane technology provides a more efficient and user-friendly method that could replace amine-based systems. Firstly, the membrane does not involve liquid chemicals such as amine that are difficult to handle and maintain (Olajire, 2010). Secondly, the footprint of a membrane separation unit is much smaller than the amine absorption tower at the same manufacturing capacity. Lastly, membrane systems are quite easy to scale up just by employing more membrane modules (Bernardo et al., 2009). Although membrane based system still have their drawbacks, like lower selectivity for CO_2, higher capital investment, additional recompression cost and so on. Membrane technology is still a promising solution for the post-combustion CO_2 capture; because the cost of membrane modules could be reduced once the production quantity increases, and selectivity problem could be solved by developing new membrane materials or employing multi-stage separation (Rezakazemi et al., 2014).

The CO_2 separation utilizing membrane separation process is driven by individual component gas permeation rate differences through a membrane barrier. Hence, membrane possess a reliable characteristic such as high permeability and selectivity, chemical and thermal resistance, resistance to plasticization, resistance to aging, cost effective, and easily incorporated into different modules minimal cost (Powell and Qiao, 2006) is desirable from industrial standpoint. Selectivity and permeability are the key factor parameter of the membrane material as it influenced the rate of permeation of the targeted gas (Meisen and Shuai, 1997). The selectivity of the polymeric membrane depends on the interaction properties of the membrane while the permeability is pressure driven. This process is energy efficient when using

an extremely selective membrane material and already a conventional process in separation of air, recovery of hydrogen, and removal of CO_2 from natural gas (pre-combustion) (Bounaceur et al., 2006).

The introduction of semi-permeable membranes in gas processing for the last two decade led to the polymeric membranes application and asymmetric membranes development with enhanced permeation rates without compromising their selectivity properties (Sridhar et al., 2007). Membranes usually have a rigid pore structure with pores on the order of angstroms which allow them to discriminate molecules on the basis of their size and shape as in Figure 1.1 where the CO_2 was able to permeate through the membrane while the retentate is the N_2 gas (Rege and Yang, 2000).

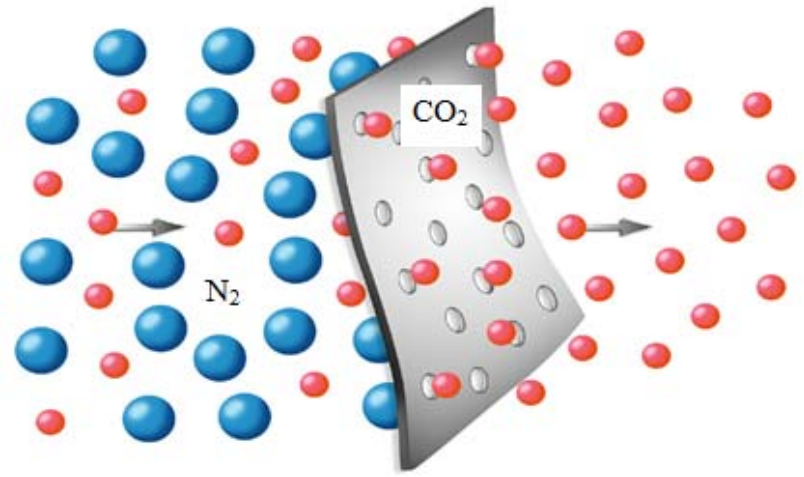

Figure 1.1: Schematic diagram of membrane for gas separation (Rege and Yang, 2000).

1.2.1 Membranes Properties for Gas Separation

The polymer is defined as a glassy polymer when the temperature is below glass transition temperature (T_g). It is hard and brittle which is related to the limited chain mobility. The movement of vibration is only allowed due to the intermolecular forces between the chains. The selectivity of the glassy polymer is very good but the